"Nanocrystalline Processing and Interface Engineering of Si_3N_4-based Nanocomposites"

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Nanocrystalline TiN Sintering and Processing

With careful powder handling procedures and processing, the nanocrystalline TiN produced in our novel reactor undergoes tremendous sintering and densification to produce dense (99%) TiN materials at 1400 °C in a simple, pressureless sintering process [1]. This quarter's efforts continued our work on the synthesis, sintering and processing of nanocrystalline TiN in three main areas. The first area was the improvement of the valved filter collection device. The second area involved a study of the microstructure which develops in the unexposed, sintered TiN materials, while the third focus was a preliminary study to begin to quantify the oxidation tendencies of these materials when they are exposed to air.

Based on the previous results for sintering the air-exposed nano-TiN powders [2], a valved filter collection device had been previously added to our reactor to allow for powder removal from the reactor without exposure to air. Efforts this quarter focused on improving the efficiency of this unit. A variety of porous metals, metal felts and polymer-based membrane materials with various pore sizes were utilized in several configurations to optimize the yield of our collection process while continuing to satisfy the gas flow and operating pressure requirements of our synthesis process. High quality nano-TiN materials can be currently collected at a rate of ≈0.4 g/hr.

In order to study the microstructure which develops upon sintering our unexposed nano-TiN, the sintered pellets were examined via SEM. This characterization verified that the TiN had sintered to full density by 1400 °C (Figure 1), while also confirming the presence of porosity in samples sintered below this temperature [3]. However, the more interesting result of this examination was the dependence of grain size (and growth) upon temperature. As shown in Figure 2, at 1200 °C, the grain size in these materials is below 35 nm. (For temperatures of 800 °C and below, the grain size was determined by XRD techniques; above this temperature, the grain size as measured on SEM fracture surfaces is plotted). While grain growth will accelerate as full density is approached, these results suggest that processing at slightly lower temperatures may allow us to produce an even finer grained TiN than our current process yields (140 nm). Therefore, we are beginning to study pressure-assisted consolidation processes with these materials. A hot isostatic pressing (HIP) process may have the additional advantage of further reducing the amount of oxygen in these materials due to the potential for an even more limited exposure to air.

In order to begin to quantify the oxidation tendencies of these high surface area nanocrystalline nitride materials, a series of oxidation experiments was conducted. Our nano-TiN and commercial, microcrystalline TiN materials were dried under a mixture of Ar

and H_2 (2.1%) to 250 °C. The materials were then heated in Ar at 5 °C/min to the oxidation temperature where they were oxidized in air with a 150 minute, isothermal soak. As shown clearly in the oxidation curves of Figure 3 (for a temperature of 400 °C), the nanocrystalline TiN oxidizes much more readily than the conventional TiN. Initial isotherm portions of these curves were used in determining an effective activation energy for this oxidation process. Figure 4 shows, in Arrhenius coordinates, the temperature dependencies of the oxidation rates (in terms of $\Delta m/m_0\tau$, where Δm is the change in weight, m_0 is the initial powder weight, and τ is the oxidation time in minutes). The effective activation energy for oxidation of the nano-TiN is 20 kJ/mol, while for the microcrystalline TiN it is 110 kJ/mol. On-going research in this area involves analysis of the reactant gas stream during this oxidation process through gas chromatography/mass spectroscopy as well as *in-situ* monitoring of the surface species during oxidation by IR techniques.

Summary

Improvements to the filter collection unit in our reactor continue to be made. An SEM/XRD grain size study has shown that our final densified TiN is nanostructured (grain size ≈ 140 nm) and that up to 1200 °C, the grain size remains under 35 nm. An oxidation study of these nanocrystalline nitride powders demonstrates further the importance of careful powder handling procedures to prevent easy oxidation of these materials in air.

References

1. J.Y. Ying, ONR Technical Report, September 30, 1996.
2. J.Y. Ying, ONR Technical Report, June 30, 1996.
3. D.T. Castro and J.Y. Ying, "Synthesis and Processing of Nanocrystalline Titanium Nitride," presented at 1996 MRS Fall Meeting, December, 1996, Boston, Massachusetts. MRS Graduate Student Award Winner.

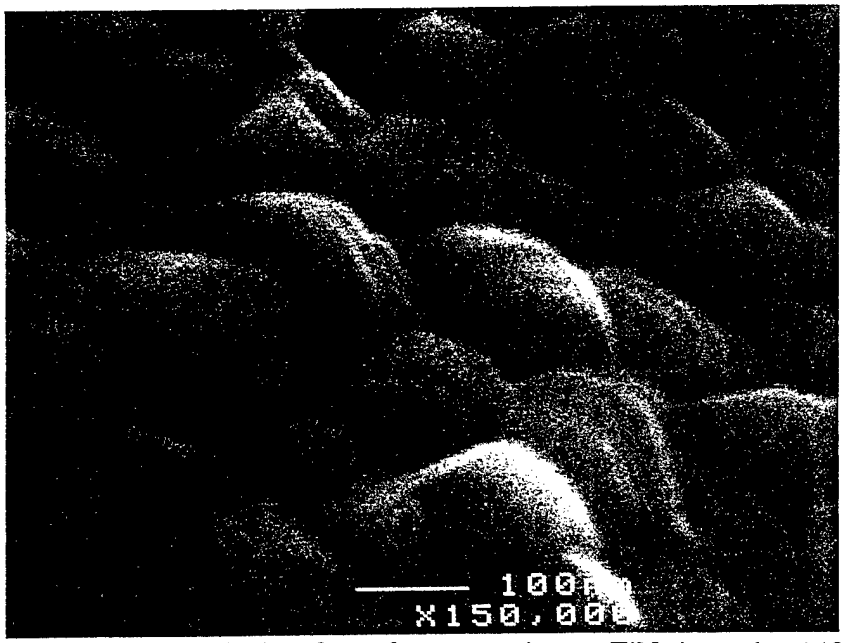

Figure 1: Thermally etched surface of unexposed nano-TiN sintered at 1400 °C.

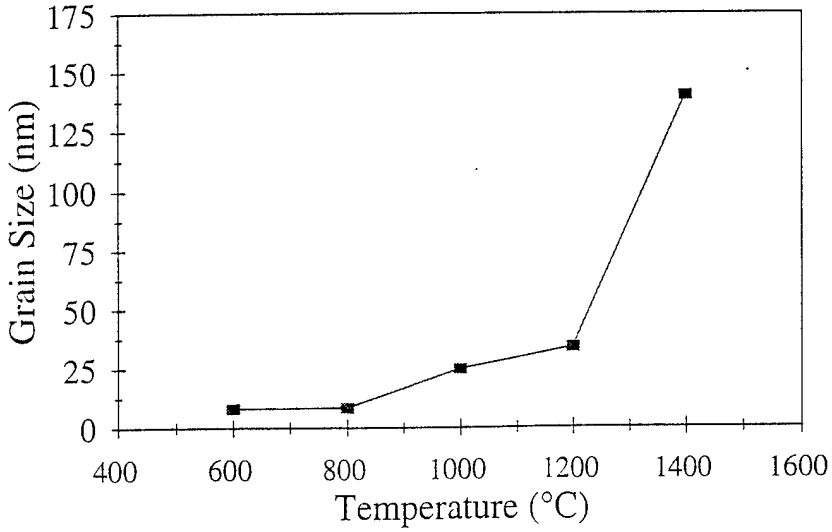

Figure 2: Grain size as a function of temperature for the unexposed, sintered nano-TiN.

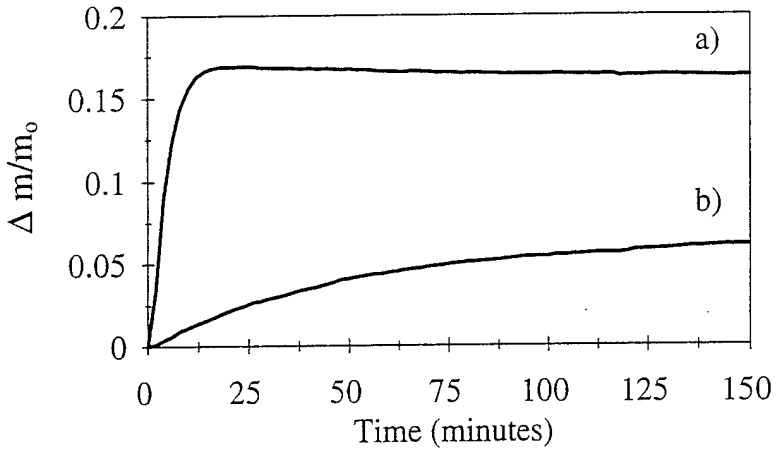

Figure 3: Oxidation in air at 400 °C of a) nanocrystalline TiN and b) microcrystalline TiN.

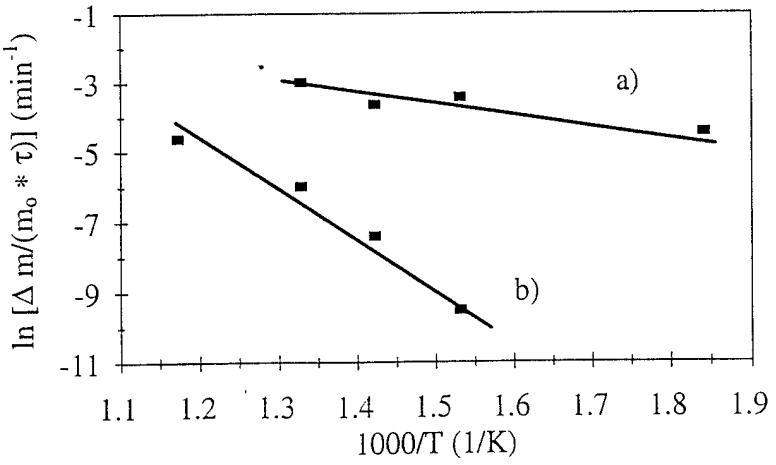

Figure 4: Temperature dependencies of the oxidation rate for a) nanocrystalline TiN and b) microcrystalline TiN.

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13. ABSTRACT (*Maximum 200 words*)

With careful powder handling procedures and processing, the nanocrystalline TiN produced in our novel reactor undergoes tremendous sintering and densification to produce dense (99%) TiN materials at 1400 °C in a simple, pressureless sintering process. This report outlines our continued work on the synthesis, sintering and processing of nanocrystalline TiN. Improvements to the filter collection unit in our reactor continue to be made. An SEM/XRD grain size study of the microstructure which develops in the unexposed, sintered TiN materials has shown that our final densified TiN is nanostructured (grain size ≈ 140 nm) and that up to 1200 °C, the grain size remains under 35 nm. An oxidation study of these nanocrystalline nitride powders demonstrates further the importance of careful powder handling procedures to prevent easy oxidation of these materials in air.

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